The Comparison between Sulfate Salt Weathering of Portland Cement Paste and Calcium Sulfoaluminate Cement Paste

Zanqun Liu [1,*], Dehua Deng [1], Geert De Schutter [2]

1 School of Civil Engineering, Central South University, Changsha, Hunan 410075, PR China
2 Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University, Ghent 9052, Belgium
Corresponding Author email: zanqun.liu@csu.edu.cn

ABSTRACT

In this paper, the damage performances of sulfate salt weathering of Portland cement paste and calcium sulfoaluminate (CSA) cement paste were compared according to authors' previous studies. It was found that the evaporation zone of specimens partially immersed in 10% Na_2SO_4 solution were both severely deteriorated for Portland cement and CSA cement. However, the differences were more significant: (1) the CSA cement paste were damaged just after 7 days exposure compared to the 5 months exposure of Portland cement paste under the same exposure condition of RH 60% and 20^{o}C; (2) the cement paste specimen was split into several pieces along the shrinkage cracks, and the damaged CSA cement paste consisted of a detachment of successive paste layers; (3) gypsum and ettringite were identified in the Portland cement paste and attributed to the paste failure mechanism, however sodium sulfate crystals were clearly observed in the detached paste layers . According to the comparison the so-called sulfate weathering of Portland cement concrete was discussed.

Keyword: Sulfate attack, salt weathering, Portland cement, calcium sulfoaluminate cement, salt weathering

INTRODUCTION

Sulfate attack on concrete is confused world [Neville A (2004)], and there are many aspects about this controversy. Nowadays there is a quite interest one that if the sulfate salt weathering or physical sulfate attack can really cause Portland cement concrete damage [Liu Z (2014)].

Sulfate attack on concrete is well known as chemical sulfate attack considered a complex physicochemical process that consists of the formation of harmful products (such as ettringite, gypsum and thaumasite) via chemical reactions, which is accompanied by the physical crystal growth of these products [Skalny JP (2001)]. Physical sulfate attack or sulfate salt weathering is generally studied in the geology community for the porous masonry damage. Obviously, concrete is also a porous material and many researchers involuntarily stated that the attention should not only paid on the chemical sulfate attack and in fact the physical sulfate attack on concrete was more common and severe than chemical sulfate attack because physical salt attack may occur even when salt concentrations in soils are low because the salts concentrate over time at concrete evaporative surfaces [Haynes H (2013)]. However, author has exhibited many disputations to question this issue according to the literatures reviews [Liu Z (2014)] as follows:

– The W/C ratio of concrete negatively correlates with the resistance against sulfate attack.
– A mere change of cementitious composition can significantly change the long-term concrete performance.

– The addition of pozzolanic material severely accelerates concrete deterioration.

– The air entraining agent shows only a minor effect on the sulfate salt weathering of concrete.

– $MgSO_4$ does not appear to damage concrete via a physical salt attack.

– The damaged concrete does not show the highest salt content.

– Sulfate crystals cannot be observed in the damaged upper part of concrete in contact with air.

– The concrete cylinders exposed to high RH show a larger damage area compared to the cylinders exposed to a low RH environment.

Therefore, author indicates that chemical sulfate attack is still the main mechanism for the damage of concrete in the evaporation zone of concrete elements [Liu Z (2014)]. However, what is the critical factor causing this disputation? Compared to the inert masonry the chemical reactions between hydration products of Portland cement paste and sulfates cannot be avoided. Then, if there is another hydraulic cementitious material whose hydration products are also inert to sulfates like masonry, the comparison between two hydraulic cementitious materials may offer more interest evidences to deeply understand this disputation. Fortunately, Calcium sulfoaluminate (CSA) cement meets this purpose.

Compared to Portland cement, the hydration products of CSA cement contain rich ettringite, C-S-H and an Al gel, but do not include the $Ca(OH)_2$ phase. When CSA cement paste is immersed in the Na_2SO_4 solution, (1) the stability of ettringite is isolated from SO_4^2; (2) even the high Na^+ concentration cannot cause decomposition of ettringite [Damidot D (1992)]; (3) the pH value of the pore solution in the CSA cement paste will not be changed by the Na_2SO_4 solution and C-S-H will remain stable; (4) the Al gel can react with Ca^{2+} and SO_4^{2-} to form ettringte in an alkaline solution [Shi C (2000)], and the stability of the Al gel will not be influenced by Na_2SO_4. In other words, without the effect of $Ca(OH)_2$ the hydration products of CSA cement are inert to Na_2SO_4. This paper presents the different performance between the Portland cement paste with the W/C ratio of 0.45 [Liu Z (2011)] and CSA cement paste with the W/C ratio of 0.45 [Liu Z (2014)] partially immersed in 10% Na_2SO_4 solution under the same exposure condition of RH 60% and 20°C.

DETERIORATION OBSERVATION COMPARISON

After 5 months partial exposure, the Portland cement paste with a W/C ratio of 0.45 were damaged. The deterioration observation of paste specimens is presented in Fig.1.

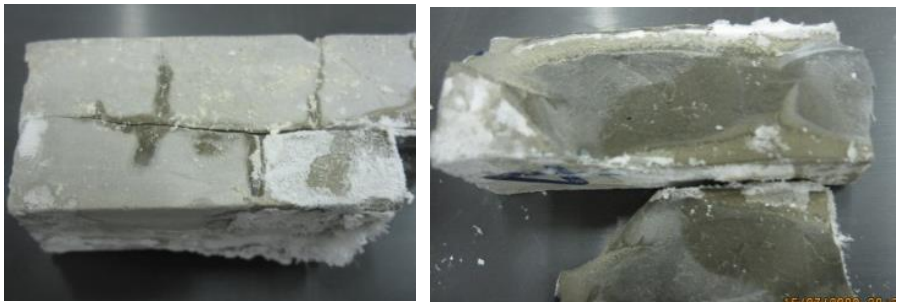

Fig.1 Visual observation of Portland cement paste specimen exposed to 10% Na_2SO_4 solution

After 7 days exposure. The deterioration image of CSA cement paste specimen is showed in Fig.2.

Fig.2 Visual observation of CSA cement paste specimen exposed to 10% Na_2SO_4 solution

Based on the visual observation, the main differences between two pastes are presented as follows:.

– The CSA cement paste was severely failed just after 7 days. The exposure time was quite shorter than 5 months exposure for Portland cement paste deterioration. It should be noticed that the damage process of sulfate salt weathering of limestone sample was also quite quick. After 8 days exposure the sample had begun to crack [Scherer GW (2004)]. Anther research [Rodriguez-Navarro C (1999)] indicated that after 30 days exposure the limestone sample was deteriorated as shown in Fig. 3.

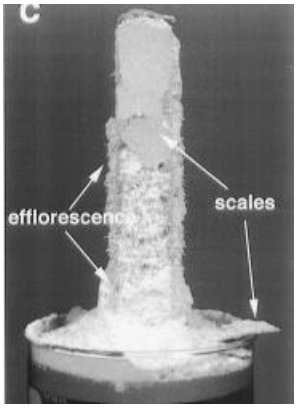

Fig. 3 Sodium sulphate crystallization at 60 per cent RH and 20 ºC for 30 days

– The CSA cement paste sample showed much more severe deterioration characterized by successive paste layers with a paste core formation. This appearance was quite similar to the typical salt weathering of porous rock [Rodriguez-Navarro C (1999)]. The Portland cement paste samples was just split into several pieces along the shrinkage cracks without surface layers scaling as shown in Fig.1, but the edge and surface of paste samples looked sound. Two different zones can be distinguished on the surface of the crack an inner dark grey zone and an outer white gray zone with white substances at the edge of the surface shown in Fig.1.

According to the above comparison, it can be sure that the damage mechanisms for these two cement pastes are different. The pore structures of these two paste may be different causing different crystallization distress, however there could not be so significant difference due to the crystallization distress on the pastes. The deterioration information of CSA paste seems more like sulfate salt weathering characterized by the quite short failure time and the successively detached paste layers.

MICRO-ANALYSIS TEST RESULTS COMPARISON

As the studies on the sulfate salt weathering of porous limestone [Rodriguez-Navarro C (1999)], to identify the sulfate crystals by means of XRD and ESEM is an ordinary and powerful evidence for crystallization distress.

Portland cement paste. As abovementioned, the products on the outer and inner zones and the white substances were identified. Figs. 4 to 8 show the ESEM, EDS and XRD analysis results. From Fig.4, it can be found that (1) the surface of the inner dark grey zone is covered by a large amount of short needle-like crystals, (2) on the right hand side of the image, a cluster of needle-like crystals stretches outwards (in the black circle). The following elements were found in the crystals using EDS: C, Na, Al, Si, S and Ca. There may be several products in the crystals. In order to further identify the products, a layer of powder scraped from the inner dark grey zone was analyzed with XRD. Fig.5 shows the XRD pattern.

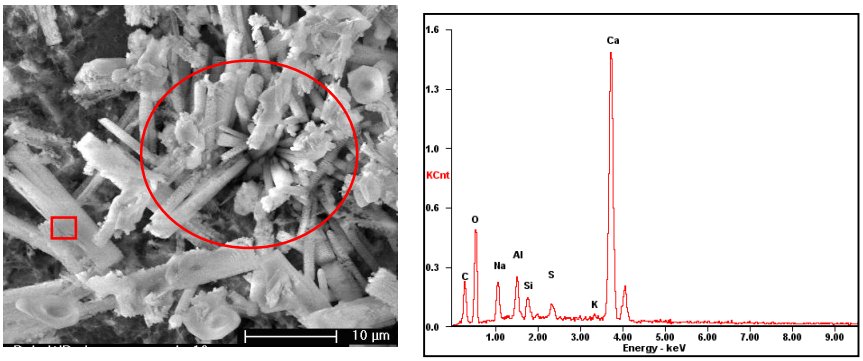

Fig.4 ESEM and EDS analysis of the products on the surface of inner dark grey zone

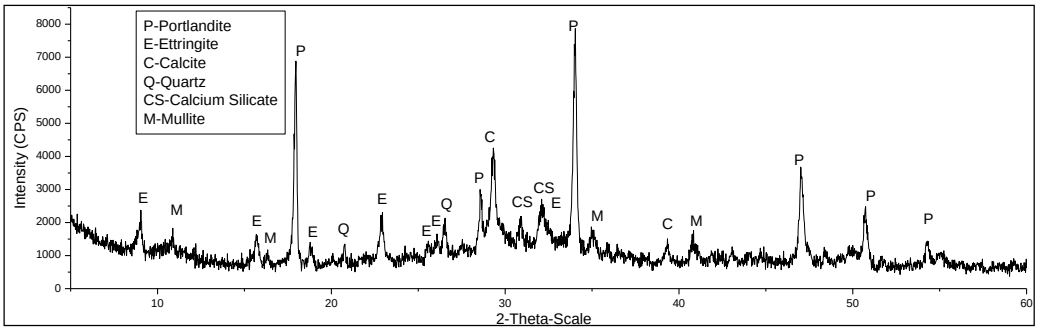

Fig.5 XRD pattern of the products in the inner dark grey zone of cement paste

According to this XRD pattern, the main products found are calcium hydroxide, ettringite and calcite. Based on the results of ESEM, EDS and XRD, the main products of the needle crystals should be ettringite and some calcite. Thenardite was not found in the inner dark grey zone.

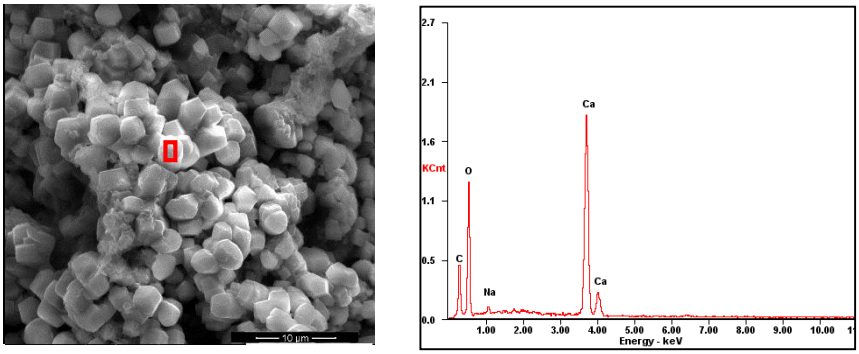

Fig.6 ESEM and EDS analysis of the products on the surface of outer white grey zone

Fig. 6 shows the ESEM image and EDS analysis of the outer white grey zone. Compared to the inner dark grey zone, the products in the outer white grey zone are relatively simple. A large amount of dense popcorn-like crystals were discovered in this zone. According to the EDS analysis, these crystals should be $CaCO_3$. A layer of powder scraped from the outer white grey zone was also analyzed by means of XRD. Fig. 7 shows the XRD pattern. Compared to Fig.5, a larger amount of calcite was formed. This means that more of the hydrated cement paste was carbonated. Fig. 8 shows the ESEM image and EDS analysis of the white crystal on the surface of the outer white grey zone. This white crystal was identified as thenardite (Na_2SO_4).

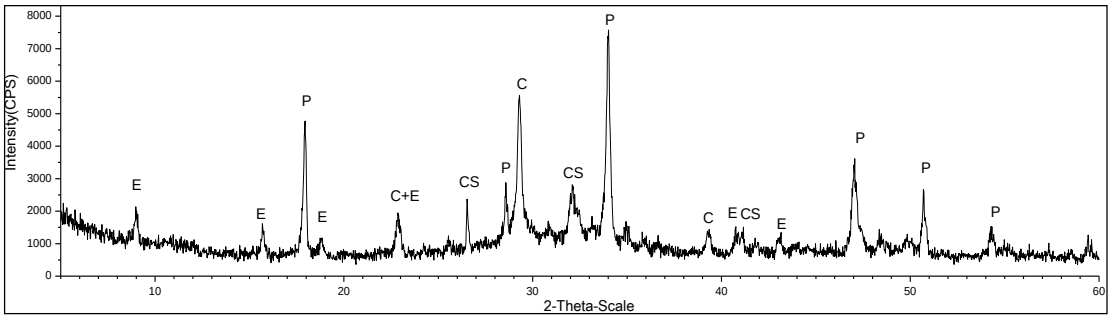

Fig.7 XRD pattern of the products in the outer white grey part of cement paste

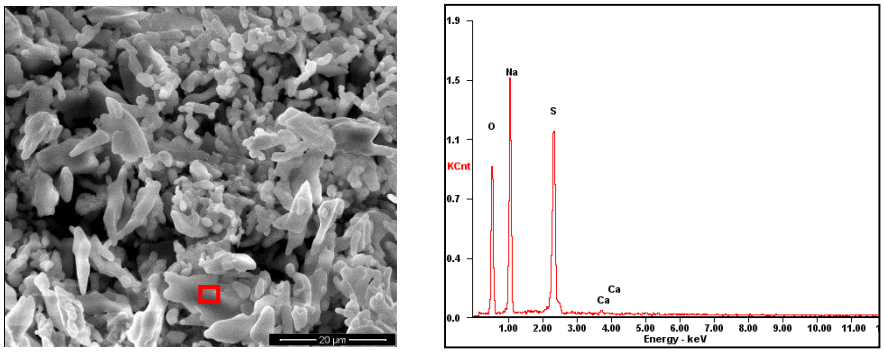

Fig.8 ESEM and EDS analysis of the white crystal on the surface of the outer zone

From the micro-analysis on the surface of the shrinkage cracks in the cement paste specimens exposed to sodium sulfate solution, the following conclusions can be drawn: (1) sodium sulfate crystals could not be identified in the cement paste; (2) crystallization of sodium sulfate occurred on the surface of the $CaCO_3$ crystals, the carbonated products of hydrated cement paste.

According to the above results, first, it is not likely that sodium sulfate crystallization is responsible for the deterioration of specimens. After the specimen is partially immersed in sodium sulfate solution, the shrinkage cracks will be filled with solution through capillary sorption. In accordance with the mechanism of crystal growth [Scherer GW (2002)], the Na_2SO_4 crystals in the crack will dissolve and diffuse to the surface when in contact with air. As a consequence there is efflorescence and crack covering (on the outer zone of the crack surface in contact with air as shown in Fig. 1). As we know, efflorescence results in little or no damage [Lopez-Acevedo V (1997), Gomez-Heras M (2007)].

With respect to ettringite attack, the large crystallization pressures are produced only in small pores (typically < 0.1 μm) [Scherer GW (2002)]. However, fracture is not caused by crystallization in a single pore. It requires crystal growth over a region comparable in size to the strength-controlling flaws [Scherer GW (1999)]. Taylor also pointed out that [Taylor HFW (2001)] ettringite

crystallization pressure develops in the nanometric pores of the paste, causing an expansion of paste and opening gaps, followed by precipitation of crystals in these gaps. In this case, ettringite crystals first form in the pores and cause expansion. Crystals can easily interact with the shrinkage crack to make them grow and cause the crack to develop, followed by the precipitation of ettringite on the surface of the cracks. In effect, in Fig.4, we can find a cluster of needle-like crystals stretch outwardly, and the growth of crystals is perpendicular to the surface of crack, apparently, this will push the paste piece away and cause the crack to develop.

Calcium sulfoaluminate (CSA) cement paste. According to Fig. 2, a small piece of the paste layer was dried and analyzed by means of ESEM, EDS and XRD. The products on the surface of the paste core were analyzed by means of ESEM and EDS. The products in the core paste were identified by means of XRD.

Fig. 9 shows the ESEM image and EDS result for products on the surface of the paste layer. A large bunch of crystals were generated on the surface of the paste layer, and could be identified as Na_2SO_4 crystals by EDS analysis.

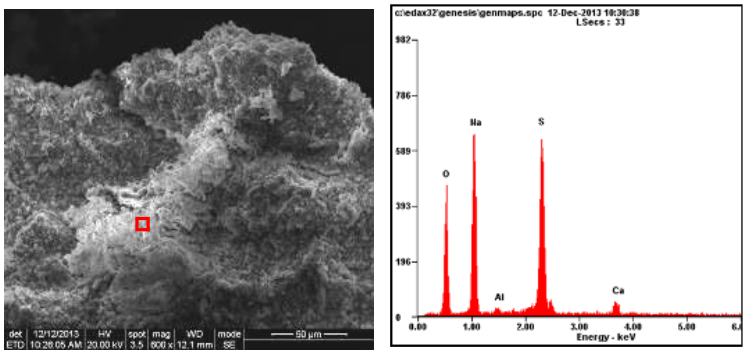

Fig. 9 ESEM image and EDS analysis of products in successive layers

Fig. 10 shows the ESEM image and EDS result of the products on the surface of the paste core. The surface of the paste core was almost covered by a layer of white crystals. These crystals can also be identified as Na_2SO_4 according to EDS analysis.

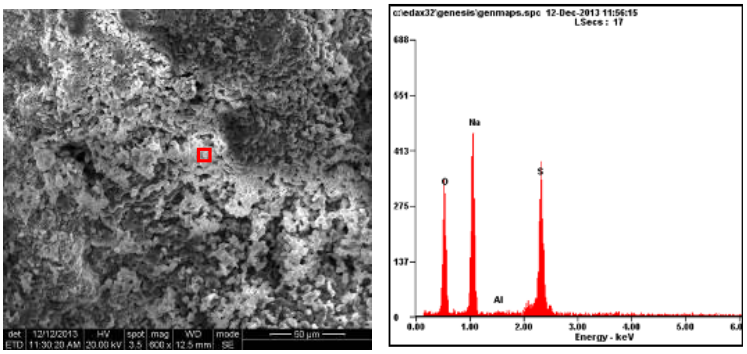

Fig. 10 ESEM image and EDS analysis of the products on the surface of the paste core

Based on the observation in Fig. 2, the paste core can be regarded as the last layer of successive paste layers after 7 days of exposure. A reasonable assumption is that the paste core would become smaller due to new layers detaching after 8 days of exposure. Obviously, Na_2SO_4 crystallization in the pores is the mechanism causing the CSA cement paste damage.

To verify the damage mechanism, the products in different parts of the paste specimen were

identified by XRD.

The effect of carbonation on the stability of CSA cement paste is a problem, and ettringite decomposes to gypsum, calcium carbonate, and alumina gel after carbonation, as described in the following equation [Nishikawa T (1992), Chen X (1994)]:

$$3CaO \cdot A1_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 = 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) + A1_2O_3 \cdot xH_2O + (26-x)H_2O \quad (1)$$

In Fig. 11, the products from the surface paste and inner paste of the top part of specimens in contact with air, but not immersed in the Na_2SO_4 solution, were identified by XRD analysis. The XRD Pattern 1# can be regarded as the reference pattern that was isolated from the sulfate solution and atmosphere. In Pattern 1#, the main phases were ettringite and unhydrated $3Cao \cdot 3Al_2O_3 \cdot CaSO_4$. However, Pattern 2# indicated that ettringite diminished when accompanying the formation of gypsum and calcium carbonate, and this result occurred even in the absence of the sulfate solution.

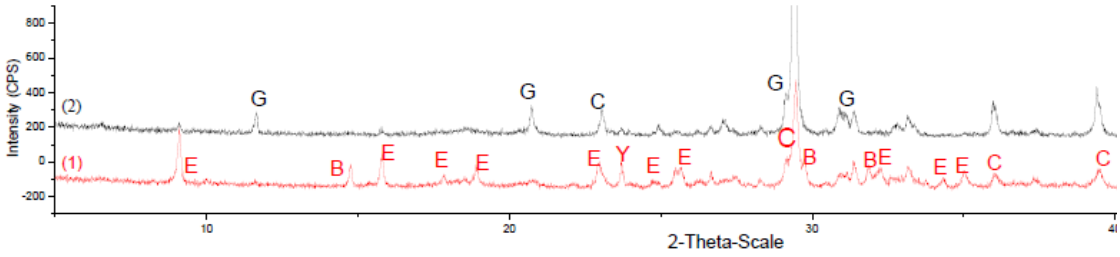

Fig. 11 XRD patterns of the surface paste and the inner paste of the top part. (1)- the inner paste of the top part; (2)-the surface paste of the top part (B-Bassanite: $CaSO_4 \cdot 0.5H_2O$; C-calcite: $CaCO_3$; E-Ettringite: $CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; G-Gypsum:$CaSO_4 \cdot 2H_2O$, Y-Yeelimite: $3Cao \cdot 3Al_2O_3 \cdot CaSO_4$)

The paste of the specimen in the sulfate solution (Pattern 3#) was also compared with the reference pattern, as shown in Fig. 12. The products in the paste were the same as the products after carbonation of ettringite as described in the literature [Nishikawa T (1992)]: calcium carbonate in the form of aragonite and gypsum. No new phase was generated in the paste in contact with the sodium sulfate solution.

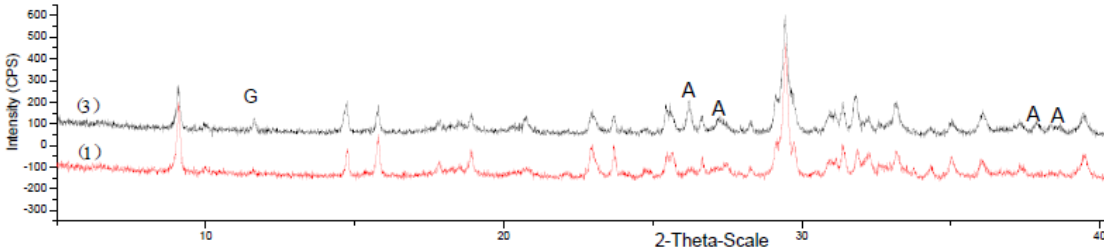

Fig. 12 XRD patterns of the paste in the sulfate solution and the inner paste of the top part. (1)- the inner paste of the top part; (3)-the paste in the solution (A-Aragonite: $CaCO_3$)

Combining the results in Figs. 11 and 12, the phase changes in the CSA cement paste immersed in the sodium sulfate solution should be influenced by carbonation but not sodium sulfate.

Fig. 13 shows the XRD patterns of the successive paste layers (Pattern 4#) and paste core (Pattern 5#).

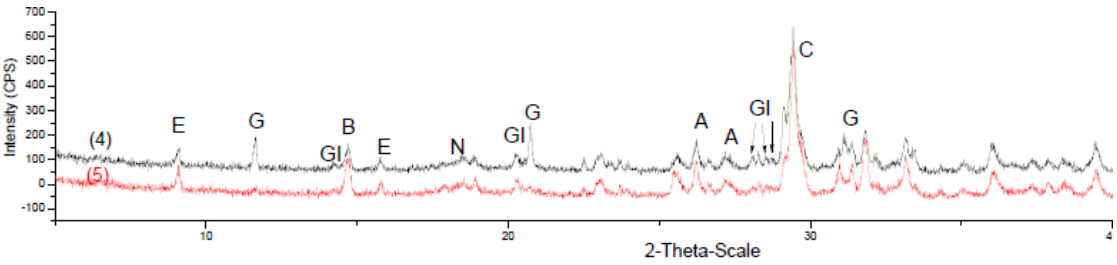

Fig. 13 XRD patterns of the successive paste layers and the paste core in the evaporation zone. (4)- the successive paste layers; (5)- paste core. (A-Aragonite: $CaCO_3$; Gl-Glauberite: Na_2SO_4 $CaSO4$; N-Sodium Sulfate:Na_2SO_4)

These results can be described as follows:

– Compared to Pattern 3#, Patterns 4# and 5# contained gypsum and aragonite, but ettringite had diminished;

– Compared with Pattern 1# and 3#, no other new phases were formed in Patterns 4# and 5# except for the sodium sulfate and double salt of glauberite (Na_2SO_4 $CaSO_4$).

– The formation of glauberite indicated that the formation of gypsum was not influenced by the sodium sulfate solution and that sodium sulfate could stably accumulate in the CSA cement paste;

– The appearance of glauberite in the evaporation zone of the damaged paste seems strange because sodium salts could not be found in the paste directly exposed to the sodium sulfate solution. The solution transport mechanisms in the different pastes were the key factors to answer this question. We know that ions penetrated into the paste when the paste was immersed in the solution, as the Na_2SO_4 concentration of the pore solution in the paste was far lower than the concentration of the external Na_2SO_4 solution. However, due to the wicking action, the concentrations of the ions in the pore solution in the evaporation zone reached super-saturation [Liu Z (2012)], causing sodium sulfate crystallization in the paste and the formation of successive paste layers. The damaged paste evidently aggravated the carbonation-induced decomposition of ettringite, causing a large amount of gypsum to form. In the pore solution with the higher concentration of sodium sulfate and gypsum, the double salt of glauberite was generated.

DISCUSSION

According to the above comparison of visual observation and micro-analysis results, the statement is clear that the Portland cement paste was suffered chemical sulfate attack and physical sulfate attack or sulfate salt weathering caused CSA cement paste deterioration. Then, what is the reason for this difference?

$Ca(OH)_2$, ettringite and C-S-H are the main hydration products of Portland cement. When cement paste is in contact with sulfate ions, (1) $Ca(OH)_2$ reacts with sulfate ions to form gypsum and causes expansion, (2) $Ca(OH)_2$ reacts with sulfate ions and Al to form ettringite and causes expansion, (3) the pH value of the pore solution is influenced by the $Ca(OH)_2$ concentration and controls the stability of ettringite and C-S-H[Santhanam M (2004)]. The source of the chemical sulfate attack on concrete seems to be $Ca(OH)_2$. In other words, the $Ca(OH)_2$ – ettringite – C-S-H – Al gel system in the Na_2SO_4 solution, is unstable due to the chemical reaction between $Ca(OH)_2$ and Na_2SO_4. However, the ettringite – C-S-H – Al gel system of CSA cement paste hydration products can exist in the Na_2SO_4 solution due to the absence of the chemical reaction between $Ca(OH)_2$ and Na_2SO_4 as discussion in introduction. In the first case, chemical sulfate attack is the failure mechanism in

the evaporation zone of concrete, whereas in the latter case, physical sulfate attack (sulfate crystallization) is the damage mechanism in the evaporation zone of concrete. These results indicate that if chemical reactions occur between sulfates and cement hydration products, sulfate crystallization in the pores will not occur and cause concrete damage.

To explain the effect of the relationship between sulfate salts and cement hydration products on the deterioration mechanism for cementitous materials, the theory of crystal growth in a pore should be reviewed. Before the important paper by Carl W. Correns was published in 1949, this author had written other papers to explain the theory of crystallization [Flatt RJ (2007)]. In 1926, he attempted to explain the relationship between interfacial tension and growth pressure: if a crystal *C* is detached from the support S, the liquid *L* will be pulled between the supporting and the loading surface and work must be carried out. An interface of size ϖ and interfacial tension γ_{cs} disappears in this process. At the same time, two new equally sized interfaces are created, which have the interfacial tensions γ_{cl} and γ_{sl}. If the crystal is elevated, including the weight added during growth, then the work required is:

$$A = \varpi.(\gamma_{cs} - \gamma_{cl} - \gamma_{sl}) \quad (2)$$

Where: ϖ is the interface size, γ_{cs} is the interface tension between the crystal and support; γ_{cl} is the interface tension between the crystal and liquid; and γ_{sl} is the interface tension between the liquid and support.

If the crystal is elevated, the following condition should be fulfilled:

$$\gamma_{cs} > (\gamma_{cl} + \gamma_{sl}) \quad (3)$$

On the contrary, if the liquid between the crystal and support disappears, the chemical potential $\gamma_{cs} - (\gamma_{cl} + \gamma_{sl})$ is the barrier. Specifically, a chemical potential proportional to $\gamma_{cs} - (\gamma_{cl} + \gamma_{sl})$ is available to prevent contact, drawing liquid into the gap between the crystal and the support. In other words, the liquid film between the crystal and particle is vital for the crystal to continue growing. The van der Waals force should act as a repulsive force within the film and between the particle or support and crystal. On the other hand, if the particle or support attracts the salt crystal, the chemical potential preventing contact will decrease and even disappear, the liquid film will disappear and the crystal will grow and contact and engulf the particles. Similarly, if the interaction between the salt crystal and pore wall is repulsive, a film between the crystal and the pore wall will form. However, if the pore wall attracts the salt, rather than repels, the salt will absorb on the pore wall. The thinner film disappears, and the crystal growth stops. This mechanism controls stress from salt crystallization [Houck J (2006)]: to avoid the damaging crystallization pressure, eliminating the repulsive forces between the growing salt and the pore wall would be sufficient. For this purpose [Houck J (2006)], certain polymers capable of anchoring to the pore wall and containing a short chain with a ligand that can strongly adsorb various types of salt can be used to alter the surface chemistry of the pore. Changing the surface chemistry of the pore can switch the interaction between the pore wall and salt crystal from repulsion to adsorption. The crystal would be attracted rather than repelled by the wall. The crystal would grow after contact with the wall, but the growth would then stop without any stress developing.

Therefore, if chemical reactions between sulfates and cement hydration products exist, the pore wall of the cement paste is attractive to the sulfates rather than repulsive, and forming a liquid film between the pore wall and the salt crystal is impossible. Crystal growth would stop without any stress developing. On the contrary, if a chemical reaction does not occur or chemical adsorption

disappears between the salt and pore wall, then the thin film between the crystals and pore wall will be formed and sulfate salt crystallization pressure would perform work. This reason explains the role of $Ca(OH)_2$ in sulfate salt weathering of Portland cement concrete. In a previous paper by the authors of the present paper [Liu Z (2011)], the occurrence of sulfate crystallization in the $CaCO_3$ crystals of the carbonated products of $Ca(OH)_2$ also attributed to the disappearance of chemical reactions between $Ca(OH)_2$ and sulfates.

CONCLUSIONS

In this paper, the damage of evaporation zones of Portland cement paste and CSA cement paste partially immersed in Na_2SO_4 solution was compared. The comparison results clearly support that chemical sulfate attack is still the main cause of Portland cement paste damage, but physical sulfate attack or sulfate salt weathering is the mechanism of the CSA paste failure.

REFERENCES

Chen X, Zou R (1994), "Kinetic study of ettringite carbonation reaction", Cem. Concr. Res. 24(7): 1383-1389.

Damidot D, Atkins M, Kindness A, Glasser FP (1992), "Sulphate attack on concrete: limits of the AFt stability domain", Cem. Concr. Res., 22(2-3): 229-234.

Flatt RJ, Steiger M, Scherer GW (2007), "A commented translation of the paper by C.W. Correns and W. Steinborn on crystallization pressure", Environ. Geol., 52(2): 187-203.

Gomez-Heras M, Fort R(2007), "Patterns of halite (NaCl) crystallisation in building stone conditioned by laboratory heating regimes". Environ Geol, 2(2):239–47.

Haynes H, Bassuoni MT (2013), physical salt attack on concrete, Concr Int;33(13):38–42.

Houck J, Scherer GW (2006), "Controlling stress from salt crystallization", Fracture and Failure of Natural Building Stones, Springer, Dordrecht, 299–312.

Liu Z, Deng D, De Schutter G, Yu Z.(2011), "Micro-analysis of "salt weathering" on cement paste", Cem. Concr. Compo. 33(1):179-191.

Liu Z, Deng D, De Schutter G, Yu Z (2012), "Chemical sulfate attack performance of partially exposed cement and cement + fly ash paste", Constr. Build. Mater. 28(1): 230-237.

Liu Z Deng D, De Schutter G, (2014), "Does concrete suffer sulfate salt weathering?", Constr Build Mater, 66: 692–701.

Liu Z, Deng D, De Schutter G, Yu Z(2014), "The role of Ca(OH)2 in sulfate salt weathering of ordinary concrete" submitted to Cem. Concr. Compo.

Lopez-Acevedo V, Viedma C, Gonzalez V, La Iglesia A (1997), "Salt crystallization in porous construction materials. II. Mass transport and crystallization processes". J Cryst Growth, 182(1-2):103-10.

Neville A (2004), "The confused world of sulfate attack on concrete", Cem Concr Res, 34(8):1275–96.

Nishikawa T, Suzuki K, Ito S (1992), "Decomposition of synthesized ettringite by carbonation", Cem. Concr. Res. 22(1): 6-14.

Rodriguez-Navarro C, Doehne E.(1999) "Salt weathering: influence of evaporation rate, supersaturation and crystallization pattern". Earth Surf Process Landforms, 24(2–3):91–209.

Santhanam M, Cohen MD, Olek J (2004), "Sulfate attack research – whither now?" Cem Concr Res, 31(8):1275–96.

Scherer GW (2004), "Stress from crystallization of salt", Cem. Concr. Res. 29(9): 1613-1624.

Scherer GW (2002), "Factors affecting crystallization pressure". International RILEM TC 186-ISA workshop and internal sulfate attack and delayed ettringite formation, Villars, Switzerland.

Scherer GW (1999) , “Crystallization in pore”. Cem Concr Res, 29(8):1347–58.

Shi C, Robert L Day (2000), Pozzolanic reaction in the presence of chemical activators: Part II. Reaction products and mechanism, Cem Concr Res. 30(4): 607-613.

Skalny JP, Odler I, Marchand J (2001), “Sulfate attack on concrete”. London: Spon.

Taylor HFW, Famy C, Scrivener KL (2001), “Delayed ettringite formation”. Cem Concr Res, 31(5):683–93.